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Controlling thin liquid film viscosity via modification of substrate surface chemistry

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Abstract

The viscosity of thin films of liquid poly(dimethylsiloxane) have been studied on silicon and fluoropolymer-coated silicon by means of a perturbation technique applied using colloid probe atomic force microscopy. The liquid film supported by a silicon substrate exhibited a greater viscosity than the bulk liquid, due to the strong interaction between the molecules near to the liquid/solid interface. In comparison, the liquid film supported by a fluoropolymer-coated substrate exhibited a similar viscosity to the bulk liquid, due to the weak interaction between the liquid and the fluoropolymer surface. This demonstrates the possibility to control the viscosity of thin liquid films via selection of the substrate chemical properties.

Keywords

poly(dimethylsiloxane), thin film, viscosity, fluoropolymer, atomic force microscopy

1. Introduction

Thin film structure and dynamics are topics of significant research interest, with applications in fields as diverse as electronics, healthcare technologies and biomedical engineering. It is well-established that the properties of ultrathin films can vary as a function of the film thickness [1-4] with polymer chain segments at the film/substrate interface exhibiting decreased mobility compared with the bulk film, whereas segments at the free surface exhibit greater mobility than the bulk film. The effect of this anisotropy affects the properties of materials which include viscosity [1], glass transition temperatures [2-3], diffusion coefficients [4], and rheological properties [5]. For systems where there was a favourable interaction between the film and the surface chemical moieties of the supporting substrate, the properties of the film differed from those of the bulk. Granick and co-workers have employed techniques such as the surface forces apparatus and extensively studied the properties of polymer melts, showing that geometric confinement reduces polymer chain mobility regardless of the presence or absence of favourable intermolecular interactions [6-8]. In cases where extreme confinement of molecules is conferred, liquid films were made to behave as if they were solids [9-10]. Similarly, researchers such as Ducker [11] and Butt [12] have used atomic force microscopy to study the lubrication behaviour, slip properties, and interfacial molecular organisation of thin liquid polymer films. Butt and co-workers have also studied the propensity of molecules to form brush-like layers at the solid/liquid interface, due to the end groups present in the molecular chains [13].

In this work, we present a simple model for assessing the viscosity of thin liquid films, and investigate the viscosities of films deposited onto different surfaces which the bulk liquid wets favourably and unfavourably. Thin films of liquid poly(dimethylsiloxane) (PDMS) were spin-cast onto silicon and fluoropolymer-coated silicon substrates. The viscosities of the liquid PDMS films were assessed via video microscopy by applying a perturbation to the surface of the film using colloid probe atomic force microscopy, and recording the time required for the surface tension-driven recovery of the perturbation. The film viscosity was calculated using an analytical solution based on a solution originally derived by Middleman [14].

2. Experimental

2.1 Rheometry

The rheological properties of a linear PDMS liquid of zero-shear rate viscosity 30 Pa.s (Dow Corning, UK) were measured as a function of shear rate using an AR-G2 rheometer (TA Instruments, UK) with a cone and plate configuration, employing a 40 mm diameter, 2° stainless steel cone. Measurements were performed at a temperature of 20°C . The molecular weight of the PDMS is approximately 80 kg/mol, which is in excess of the 34 kg/mol critical entanglement molecular weight for PDMS [15]. The radius of gyration of the PDMS is approximately 18 nm, according to the relationship reported by Silberzan and Leger [16] and Valignat *et al.* [17]. Figure 1 shows the measured properties, in which it can be seen that the PDMS has a constant viscosity at shear rates $< 50\text{ s}^{-1}$; this is the upper Newtonian plateau. At shear rates $> 50\text{ s}^{-1}$ the liquid undergoes shear thinning, with the lower Newtonian plateau occurring at shear rates $> 10^3\text{ s}^{-1}$.

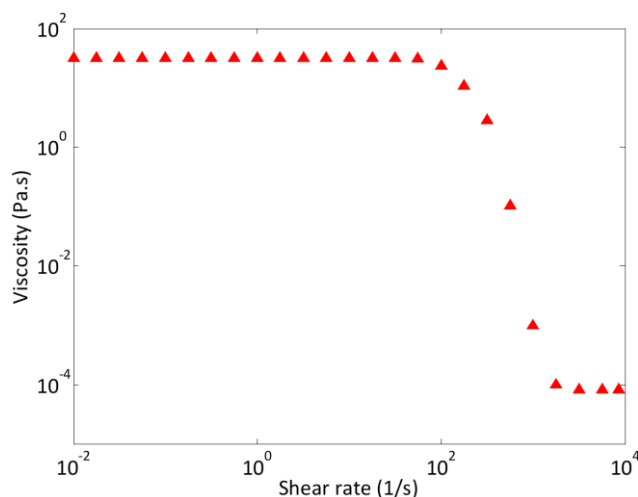


Figure 1. Viscosity of PDMS liquid as a function of shear rate using cone and plate rheometry

2.2 Preparation of CF_xO_y films

Solid CF_xO_y films were deposited by plasma polymerisation onto the polished side of single crystal N-type Si (100) wafers (IDB Technologies, UK) using a STS Multiplex ICP DRIE etcher (STS Plc., UK), utilising C_4F_8 gas (Pelchem, South Africa) at a flow rate of 80 sccm. The platen power was set to 600 W and the deposition time was 60 s. Wafers were used as received, with any visible dust or debris being removed by sweeping the surface with N_2 gas.

2.3 Preparation of PDMS films

PDMS liquid of 30 Pa.s zero-shear rate viscosity was dissolved in HPLC grade toluene (Fisher Scientific, UK) at a concentration of 2 % w/w. The solution was allowed to equilibrate for 48 h to ensure complete dissolution. A 50 μL droplet of solution was dispensed using a fixed needle syringe (Hamilton, UK) onto the substrate of interest, immediately prior to spin coating (WS-400E-6NPP-Lite, Laurell Technologies, USA), yielding a thin film of PDMS liquid following evaporation of the solvent. The first type of substrates was a clean Si wafer with a 2 nm native SiO_2 surface oxide layer, which is hereafter referred to as a Si/ SiO_2 . The second type of substrate was a solid CF_xO_y film deposited on a clean Si/ SiO_2 wafer, which is hereafter referred to as the CF_xO_y film.

2.4 Characterisation of Si surface and CF_xO_y film surface

The thickness of PDMS liquid films and CF_xO_y films was measured using a UVISSEL ellipsometer (Jobin-Yvon/Horiba, UK) over the wavelength range 250-800 nm and at an angle of incidence of 70° . Calculation of the film thickness was performed for each measurement, based on a four-phase ambient/ CF_xO_y film/ SiO_2 /Si model, or a five phase ambient/PDMS/ CF_xO_y film/ SiO_2 /Si model in which each layer was assumed to be isotropic. The roughness of the Si surface and CF_xO_y film surface was measured using a NanoWizard II atomic force microscope (AFM, JPK, UK) operating in Intermittent Contact Mode under ambient conditions, employing rectangular pyramidal-tipped Si cantilevers (RTESP, Veeco, UK) with a nominal tip diameter of 50 nm. Extensive details regarding the characterisation of CF_xO_y thin films have previously been described by Cheneler *et al.* [18]. CF_xO_y films deposited

on Si substrates were found to exhibit similar surface roughnesses to the underlying substrate, with R_a values of the order 1 nm.

2.5 Contact angle measurement

The contact angle behaviour of a droplet of PDMS liquid on the Si surface and CF_xO_y film surface was measured using a purpose-built apparatus employing a Charge-Coupled Device (CCD) KP-M1E/K camera (Hitachi, UK) and FTA Video Analysis software v2.0 (First Ten Angstroms, UK).

2.6 Film perturbation

An indentation was made in PDMS liquid films deposited onto the Si surface and CF_xO_y film surface using a rectangular Si cantilever with an attached spherical SiO_2 colloid probe, radius 6 μm , at its apex (NovaScan, USA). A compressive load of 300 nN was applied to the film for approximately 5 s before rapid retraction of the probe. The cantilever spring constant was 20.1 N/m and was calibrated according to the method described by Bowen *et al.* [19]. The cantilever was housed in a MultiMode AFM (Veeco, UK) operating an 'E' scanner, and images were recorded from the white light video system built into the AFM using an analog-to-digital USB video converter (BRSL, UK). Images of the film were captured every 30 s. The recovery of the perturbation was monitored over a period of 2 h to ensure full recovery had been achieved. Three measurements were performed for each liquid/solid combination. The theoretical basis from which the film viscosity is calculated following a measurement is described in §3.

3. Film perturbation theory

Middleman derived an analytical solution to the problem of the levelling of a surface disturbance to a liquid thin film [14]. Fig. 2 shows a schematic of the system. The solution is based on the assumption that the shape of the disturbance can be described by a sinusoidal function. Given that the disturbance is applied using a spherical colloid probe, and assuming axisymmetry in the radial direction, the solution takes the form:

$$H(r) = \bar{H} + h\sin(kr) \quad (1)$$

where $H(r)$ is the height of the liquid film above the substrate, r is the radial coordinate, \bar{H} is the mean film thickness, h is the amplitude of the disturbance, and k is the wavenumber of the disturbance, which is equal to $2\pi/\lambda$, where λ is the wavelength of the disturbance.

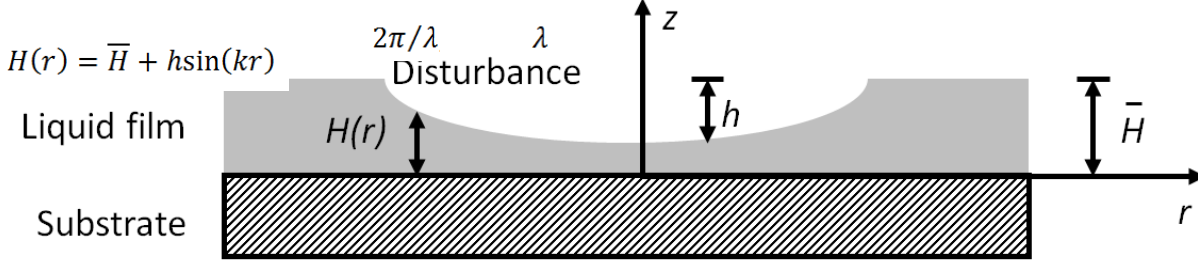


Figure 2. System geometry under consideration

In order to obtain an analytical solution, the following assumptions are made:

1. The lubrication approximation applies, which states that the velocity field contains only radial flow.
2. The liquid exhibits Newtonian behaviour.
3. Inertial terms and gravitational terms are neglected, as the system has low mass.
4. Surface tension provides the dominant force for restoration of the perturbed volume.
5. A no-slip boundary condition is assumed at the liquid/substrate interface.
6. There is no shear stress at the liquid/air interface.

The amplitude, or depth, of the disturbance is shown to decay exponentially, according to Eq. 2:

$$h = h_0 e^{-\beta t} \quad (2)$$

where β is the disturbance decay rate and takes the form:

$$\beta = \frac{\sigma k^4 \bar{H}^3}{3\mu} \quad (3)$$

where σ is the liquid surface tension, and μ is the liquid viscosity.

Here, the time taken for surface disturbances applied to thin liquid films to recover is monitored using video microscopy. The film thickness change is visualised via the change in colour of the thin liquid film, examples of which are shown in Fig. 3-4. The wavenumber of the disturbance was estimated using the effective wavelength of the disturbance, which was assumed to be twice the perturbation diameter, which was measured from the video images recorded. The reduction in disturbance amplitude was assumed to be 99 %. i.e. $h/h_0 = 0.01$.

Substituting Eq. 3 into Eq. 2 and rearranging for μ yields an expression for the effective viscosity of the thin liquid film, Eq. 4.

$$\mu = -\frac{\sigma k^4 \bar{H}^3 t}{3 \ln\left(\frac{h}{h_0}\right)} \quad (4)$$

$$\mu = -\frac{\sigma k^4 \bar{H}^3 t}{3 \ln\left(\frac{h}{h_0}\right)} \quad h/h_0 = 0.01$$

4. Results

Fig. 3 shows the recovery of a disturbance applied to a 264 nm film of 30 Pa.s PDMS on Si. The disturbance diameter is 19.5 μm . Fig. 3(a) shows the appearance of the film 10 s after application; fig. 3(b) shows the partially recovered film after 15 min; fig 3(c) shows the recovered film after 55 min. The colour of the disturbance changes until it matches the colour of the surrounding unperturbed film, and is considered recovered after 55 min. The three measurements performed yielded recovery times of 40 min, 43 min, and 55 min. Therefore, using Eq. 4, the viscosity of the Si-supported liquid film was calculated to be 50 ± 10 Pa.s.

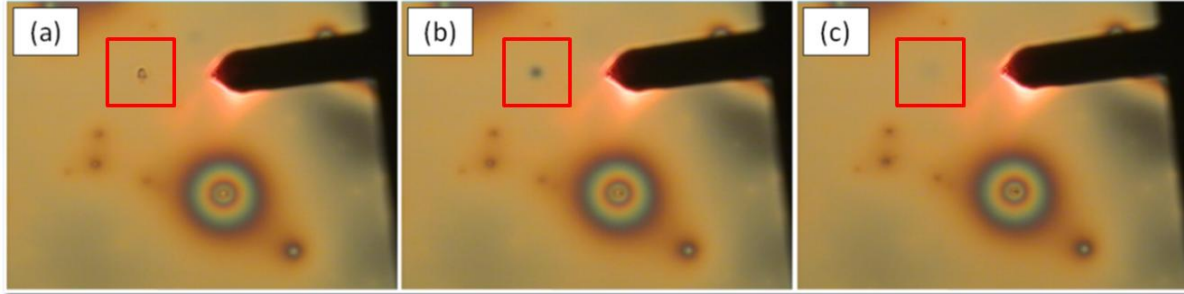


Figure 3. Application and recovery of a disturbance applied to a 264 nm thickness liquid film of 30 Pa.s PDMS on a Si substrate; (a) 10 s, (b) 15 min, (c) 55 min. The region highlighted by the red square contains the disturbance.

Fig. 4 shows the recovery of a disturbance applied to a 246 nm film of 30 Pa.s PDMS, deposited on the CF_xO_y film. The disturbance diameter is 18.9 μm . Fig. 4(a) shows the appearance of the film 10 s after the disturbance was applied; fig. 4(b) shows the partially recovered film after 6 min; fig. 4(c) shows the recovered film after 33 min. As in Fig. 3, the colour of the disturbance changes until it matches the colour of the surrounding film. The three measurements performed yielded recovery times of 27 min, 29 min, and 33 min. Therefore, using Eq. 4, the viscosity of the CF_xO_y -supported liquid film was calculated to be 30 ± 3 Pa.s.

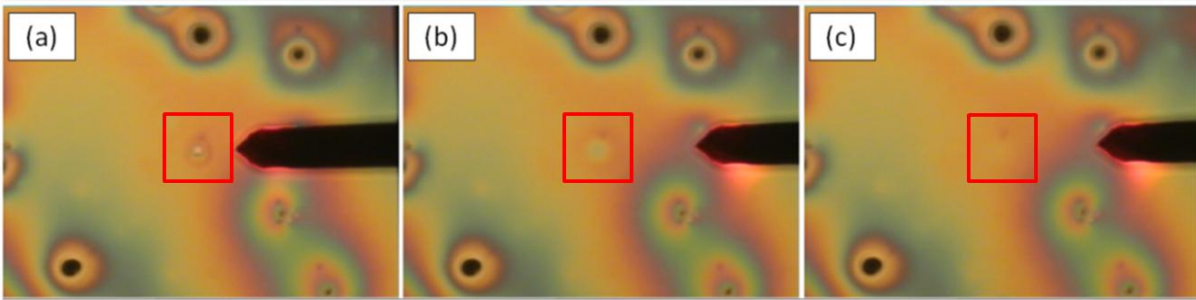


Figure 4. Application and recovery of a disturbance applied to a 246 nm thickness liquid film of 30 Pa.s PDMS on a CF_xO_y substrate; (a) 10 s, (b) 6 min, (c) 33 min. The region highlighted by the red square contains the disturbance.

5. Discussion

5.1 Interpretation of results

The viscosity of the PDMS film deposited on Si was calculated as 50 ± 10 Pa.s, which is 20 Pa.s higher than the bulk PDMS liquid viscosity of 30 Pa.s. This increase in viscosity is due to attractive intermolecular interactions between the PDMS molecules and the Si substrate surface SiO_2 . These attractive interactions decrease the mobility of the PDMS chains and hence increase the film viscosity. The spontaneous spreading of a PDMS droplet on Si indicates that the interaction between these materials is highly favourable, with PDMS chains adsorbing strongly at the interface, as has previously been reported [12, 20-21]. In comparison, a PDMS droplet deposited on the CF_xO_y film exhibited a 40° contact angle, suggesting that the interaction between PDMS chains and the CF_xO_y film is less favourable than the interaction between PDMS and SiO_2 . The viscosity of the PDMS film deposited on the CF_xO_y film was calculated as 30 ± 3 Pa.s, a value similar to the bulk PDMS liquid viscosity. This suggests that the interaction between the PDMS chains and the countersurface is minimal, allowing surface tension-driven flow to occur unhindered post-perturbation.

These results demonstrate that by controlling the chemical properties of the countersurface on which thin liquid films are deposited, flow properties comparable to those of the bulk liquid can be achieved. Selective tailoring of surface moieties, which can be achieved using self-assembled monolayers for example, affords the opportunity to specify the liquid film viscosity. These studies will be the subject of future work. It is also required that the long-term stability of thin liquid films deposited on surfaces which the bulk liquid does not fully wet is investigated, as the possibility exists that such films may be thermodynamically unstable, and dewetting could occur over extended timescales.

5.2 Advantages and disadvantages of the viscosity measurement method

The method described in §2.6 and §3 for measuring the liquid film viscosity is easily implementable and simple to perform. Here we used colloid probe AFM to apply a perturbation to the film, but it would also be possible to employ any other suitable apparatus for applying a perturbation, provided an imaging system was present to monitor the recovery. The perturbation recovery was monitored here by virtue of the change in colour of the film, due to it being of nanoscale thickness and deposited on Si. The 768×640 pixel density of the camera employed determined the resolution with which the dimensions of the perturbation could be estimated, which then impacts upon the value of the wavenumber used in Eq. 4. For the systems considered in this work, the disturbance diameters were in the range $19\text{--}21\text{ }\mu\text{m}$, which corresponded to an uncertainty of ± 3 Pa.s in the film viscosity. Hence, the film thickness, the optical properties of the liquid and the countersurface, the perturbation size, the type and capture rate of the visualisation system are all important parameters which should be considered during the design of experiments similar to those presented here. Film thicknesses greater than $1\text{ }\mu\text{m}$ could pose challenges for white light systems, although the use of an interferometric technique may provide an alternative method of visualising and monitoring perturbation dimensions and recovery.

6. Conclusion

Thin films of liquid poly(dimethylsiloxane) have been deposited on silicon and fluoropolymer-coated silicon surfaces and their viscosities calculated via the application of a perturbation technique. The liquid film supported by a silicon substrate exhibited a greater viscosity than the bulk liquid. This is due to the strong interaction between the molecules near to the liquid/solid interface. In contrast, the liquid film supported by a fluoropolymer-coated silicon substrate exhibited a similar viscosity to the bulk liquid. This is due to the weak interaction between the liquid and the fluoropolymer surface. The possibility to control and tailor the effective viscosity of thin liquid films through careful selection of the countersurface chemical properties has been demonstrated.

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